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A PREDICTION MODEL OF THE DEPTH-OF-DISCHARGE EFFECT ON THE CYCLE LIFE OF A STORAGE CELL

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Abstract

Cycle life requirements are very high for batteries used in aerospace applications in low earth orbit. The data base required to establish confidence in a particular cell design is thus both extensive and expensive. Reliable accelerated cycle life testing and performance decay modeling represent attractive alternatives to real-time tests of cycle life. In light of certain long-term cycle life test results, this paper examines a very simple performance decay model developed earlier. Application of that model to available data demonstrates a rigid relationship between a battery's expected cycle life and the depth of discharge of cycling. Further, modeling analysis of the data suggests that a significantly improved cycle life can be obtained with advanced components, materials, and designs; and that cycle life can be reliably predicted from the results of accelerated testing.

I. Introduction

For many advanced aerospace and electric vehicle applications, where mission life requirements cannot be compromised, high energy density of storage cells is critical. Since a battery's energy density is directly proportional to the depth of discharge (DOD) of cycling, and battery cycle life decreases rapidly as DOD is increased, it is important to quantify the relationship between cycle life and DOD. Knowledge of that relationship would permit one to predict the cycle life of batteries cycled at shallow DODs from data on accelerated cycling at deeper DODs. Shallow DODs are often required to support a long mission life.

Several prediction models relating cycle life to DOD have been reported.¹⁻⁶ All are briefly discussed in this paper, and one is shown to be consistent with available cycle life data on cells that failed because of a gradual wearout mode, as opposed to catastrophic failure mechanisms. We are most interested in gradual decreases in capacity because they are by nature predictable and undoubtedly related to DOD; sudden failures, on the other hand, cannot be predicted and therefore cannot be modeled.

II. Prediction Models

Several equations have been proposed for predicting battery cycle life¹⁻⁴ as a function of DOD as well as other parameters such as temperature, recharge ratio, charge rate, and discharge rate. The most popular one is

$$\ln L = A - \alpha D' \quad (1)$$

which can be transformed into

$$L = L_0 e^{\alpha(1-D')} \quad (2)$$

where L is cycle life, D' ($0 \leq D' \leq 1$) is the value of DOD, and α , A , and L_0 are constants. The values of A and L_0 can be affected by temperature and recharge ratio.^{2,3} A model (not shown here) similar to equation (1) but with an additional term for charge and discharge rate effects³ was suggested for application to data from the cycle life testing of a series of Ni/Cd cells.

The following equation for analysis of Ni/Cd cell data was also proposed:

$$L = B \frac{1 - D'}{D'} \quad (3)$$

where B is a constant and D' is depth of discharge as a fraction of actual capacity. This model assumes that the initial measured excess capacity ($1 - D'$) over the cycled value (D') is decreased at a rate of D'/B per cycle. Thus, the cell will fail to cycle when the capacity is reduced by $1 - D'$.

A similar model, including a new term (F) to represent excess capacity over the rated value, was suggested recently for cycle life limited by gradual wearout:^{5,6}

$$L = \frac{1 + F - D}{RD} \quad (4)$$

where F is the excess capacity over the rated value (in units of the rated capacity), D is depth of discharge as a fraction of rated capacity, and R is a constant.

Equation (4) is essentially the same as equation (3) in physical implications.

However, equation (4) has the advantage of requiring only the rated, rather than the actual, value of capacity to fit data. The unequivocal value of actual capacity is not usually known, whereas the rated value is always available. This paper shows that equation (4) is consistent with existing cycle life data on storage cells that failed as a result of gradual wear-out, but not catastrophic events such as shorts and other mechanical problems.

III. Physical Implications of Proposed Model

The proposed model, equation (4), for predicting the effect of DOD on cycle life assumes that the initial normalized excess available capacity $(1 + F - D)$ over the normalized capacity being cycled (D) is decreased by a fractional amount RD per cycle. The term R may be viewed as a constant associated with the rate of capacity loss. It is expressed in units of reciprocal cycles. The term F is the fractional excess capacity over the nominal capacity and thus should not be affected by cycling conditions. (For further details, consult Refs. 5 and 6.)

However, R will be influenced by parameters such as temperature, cycling regime, electrolyte composition (e.g., KOH concentration), impurities or additives in the electrolyte, amount of electrolyte in a starved cell, and chemical reactions (e.g., corrosion reactions, separator degradation). When a chemical reaction rate constitutes a substantial portion of R , equation (4) will be applicable only for a continuous cycle life test, because any long interruption would allow chemical degradation without cycling.

When the natural log of cycle life L is plotted against depth of discharge D , equation (4) will yield a nonlinear sigmoid-type curve.⁵ However, the midportion ($D > 0.2$; $1 + F - D > 0.2$) of the curve is roughly linear with a tangential slope, s :

$$s = \frac{d(\ln L)}{dD} = \frac{-(1 + F)}{D(1 + F - D)} \quad (5)$$

For example, the slope at $D = 0.5$ is -4.0 when $F = 0$, -3.43 when $F = 0.2$, and -3.0 when $F = 0.5$. The value of the slope for failure due to gradual wearout should be between -4.0 and -3.0 because F should be greater than 0 but is not likely to exceed 0.5 in an actual cell. A typical value of F for an aerospace Ni/Cd cell is about 0.2. The slope at $D = 0.5$ should be numerically similar to α of equations (1) and (2), since both s and α are the slopes of plots of $\ln L$ as a function of DOD.

IV. Test of Model against Cycle Life Test Data on Ni/Cd Cells

The proposed model, equation (4), was tested against data from two separate analyses of Ni/Cd cell cycle life. One cycle life testing program, conducted by the Naval Weapons Support Center, evaluated parametric effects on the cycle life of a large group of Ni/Cd cells containing nylon separators.^{7,8} The other, conducted by Hughes Research Laboratories (HRL), tested Ni/Cd boiler plate cells with polymer-reinforced zirconia separators.^{9,10}

Figure 1 compares cycle life data from Ref. 7, Fig. VI-4, with a linear regression on those data points and a nonlinear cycle life prediction curve calculated using equation (4). The best curve fit was obtained with $F = 0.2$ and $R = 3.5 \times 10^{-4}$. Both the prediction curve and the linear regression line closely match the experimental data.

Figure 2 compares similar data at various temperatures, from Fig. VI-6 of Ref. 7, with prediction curves having $F = 0.2$ and various values of R . Again, all curves in the figure fit fairly well to the corresponding data points; though the linear regression lines are not shown in Fig. 2, they also closely approximate the relevant data points.

The close fit of predicted to actual values when excess capacity F is held constant, as in Figs. 1 and 2, is consistent with the physical implication of the model that F should not be affected by cycling conditions. Since all test cells were from a single manufacturing series, their F value should be independent of test conditions. In both Fig. 1 and Fig. 2, the tangential slope [s of equation (5)] of all curves at $D = 0.5$ was -3.43 . That value agrees with the reported value^{2,3} of -3.8 for α of equation (1) for the same test data. (The value of α is expected to be slightly greater than that of s .) This agreement indicates that both equations (1) and (4) fit the test data points within an experimental error.

The second set of cycle life data was derived from tests of Ni/Cd boiler plate cells with polymer-reinforced zirconia separators, which are chemically stable in KOH electrolyte. Such cells differ from those with nylon separators¹¹ in that they do not suffer from separator degradation - a primary cause of cell failure. Therefore, for the improved cells, the value of R in equation (4) should be considerably less than that for the cells employing nylon separators.

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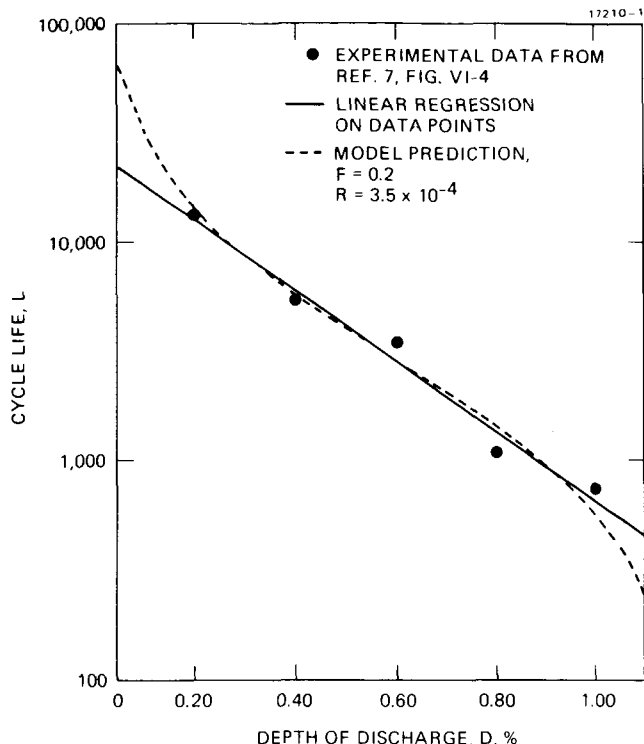


Fig. 1 Cycle life versus DOD of Ni/Cd cells containing nylon separators: experimental values taken at 40°C.

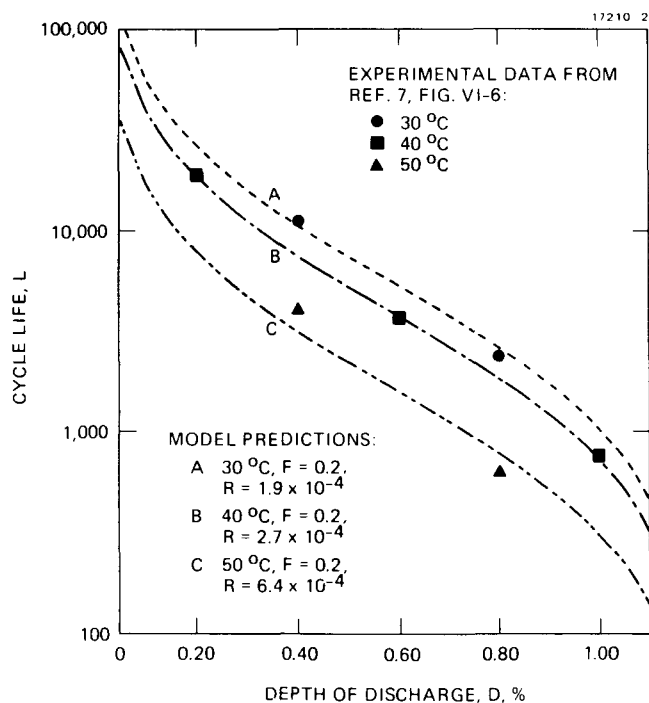


Fig. 2 Cycle life versus DOD of Ni/Cd cells containing nylon separators: experimental values taken at 30°C, 40°C, and 50°C.

The cycle life testing of the improved cells using zirconia separators was carried out in two different series. One involved type A cells containing chemically deposited nickel and cadmium electrodes. The type A cells were tested in a cycling regime consisting of a 16 min discharge at a 1.5 C rate followed by a 24 min recharge at the same rate.

The other test series involved type B cells, in which the nickel electrodes were deposited electrochemically, though the cadmium electrodes were of the same lot as those in the type A cells and thus were deposited chemically. The two different types of nickel electrodes had similar values of measured capacity as well as the same rated capacity. The type B cells were tested in a cycling regime consisting of a 30 min discharge, either at a 1.2 C rate to 60% DOD or at a 1.6 C rate to 80% DOD; followed by a 40 min recharge at the same rates, respectively, and a 2 min trickle charge at C/20 to C/15 rates. Cycle life values were taken when the end-of-discharge voltage reached 0.5 V.

The following table summarizes the test data on the zirconia-separator cells, excluding those that failed because of a short formation. The data points for the two different types of cells (A and B) were not strictly comparable in either their design or the details of their cycling regime. Nevertheless, we decided to test the model using both sets of data because we believed that the difference between them would prove to be minor. However, the data points were not numerous enough to permit even a three-point comparison with prediction plots of the cycle life as a function of the DOD at a given temperature. Therefore, the two missing data points were estimated using an extrapolation method, described below.

Figure 3 plots the logarithmic values of cycle life at various depths of discharge and temperatures against $1/T$. A three-point plot of experimental data on 40% DOD (curve A) yielded a straight line with a slope corresponding to an activation energy of 11 kcal/mole. We assumed the same activation energy value for 60% and 80% DOD. Extrapolating from that value, we obtained curves B and C for 60% and 80% DOD, respectively. From curves B and C, cycle lives of 20,500 at 60% DOD and 25°C and 4,000 at 80% DOD and 40°C, respectively, could be projected so as to produce enough estimated data points to permit a three-point comparison with prediction curves representing the effect of DOD on cycle life.

Figure 4 plots both the actual (from the table, above) and the extrapolated (from Fig. 3) data points against DOD and compares them with curves predicted using equation (4). The best fitting value of F was 0.19, indicating that the zirconia-separator cells had an excess capacity of

Table. Cycle life of Ni/Cd cells with polymer-reinforced zirconia separators at various depths of discharge and temperatures

Cell Type	Number of Cells	Depth of Discharge (%)	Temperature (°C)	Average Cycle Life
A	2	40	25	43,100
A	2	40	40	15,200
A	3	40	50	10,300
B	1	60	40	8,300
B	1	80	25	9,500

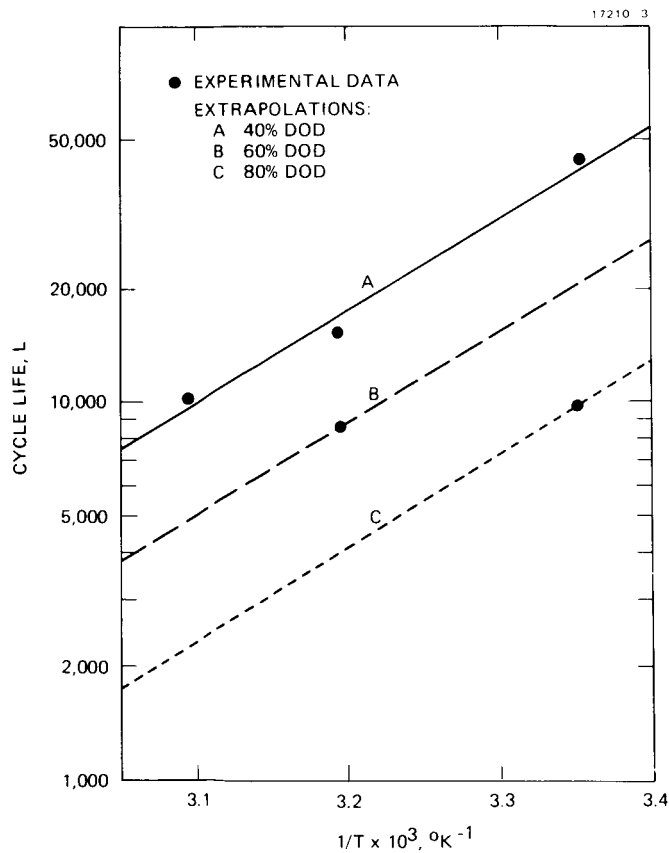


Fig. 3 Cycle life versus $1/T$ of improved Ni/Cd cells containing zirconia separators.

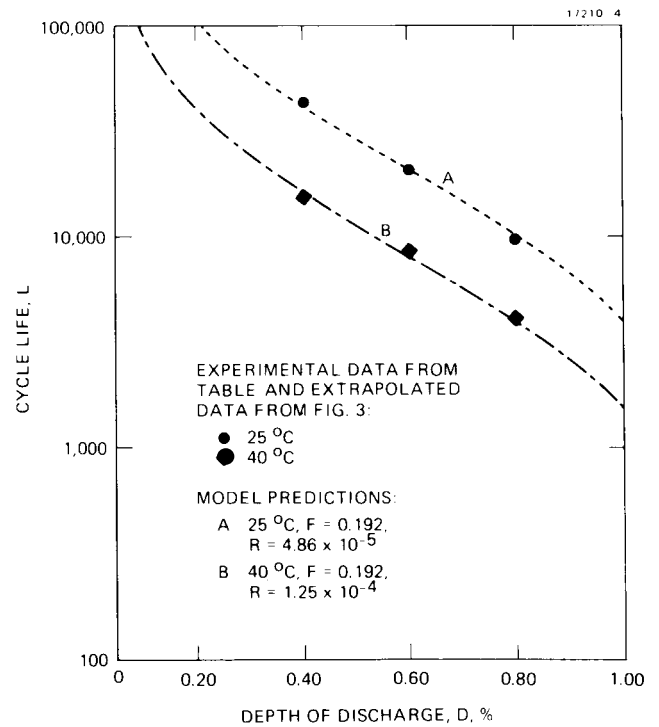


Fig. 4 Cycle life versus DOD of improved Ni/Cd cells containing zirconia separators.

19% over the rated value. The best fitting values of R were 4.86×10^{-5} at 25°C and 1.25×10^{-4} at 40°C , for curves A and B, respectively.

The prediction curves with a single F value of reasonable magnitude fit remarkably well to the experimental values, despite the inhomogeneity of data points discussed above. The value of R (1.25×10^{-4}) at 40°C is less than half that of cells using nylon separators (2.7 to 3.5×10^{-4}) at the same temperature. Those relative magnitudes of R values are also consistent with the observation that the zirconia-separator cells had much longer cycle lives than those containing nylon separators.¹⁰ Thus, the proposed model, equation (4), appears to represent the experimental data quite well.

V. Test of Model against Cycle Life Test Data on Li/MoS₂ Cells

The proposed model, equation (4), was also applied to cycle life test data on Li/MoS₂ cells that are reported to have failed gradually.¹² Figure 5 compares cycle life data from Ref. 12, Fig. 4, with a linear regression on those data points and a nonlinear cycle life prediction curve calculated using equation (4). The best curve fit was obtained with $F = 0.20$ and $R = 1.14 \times 10^{-3}$. In this case, the prediction curve matches the experimental data more closely than does the linear regression line, indicating that equation (4) describes the effect of DOD better than equation (1).

VI. Discussion

The proposed model, equation (4), for predicting the effect of DOD on the cycle life of a storage cell seems to closely approximate available cycle life data on Ni/Cd and Li/MoS₂ cells that appeared to have failed owing to gradual wearout, though the data points are too few to be statistically significant. The values of F (0.19 to 0.20) used in our calculations produced curves that fit the corresponding data quite well, consistent with the physical implication of the model that F should not be affected by cycling conditions.

The other model, equation (1), also fit the same data, as reported by earlier investigators.^{2,3} Overall, however, equation (4) appears to fit better than equation (1), especially for the data on Li/MoS₂ cells at high DOD, as shown in Fig. 5. Though equation (4) is not perfect, and additional data are needed to conclusively test the validity and relative merits of these two prediction models, equation (4) seems to be the more straightforward.

We did not test the proposed model against cycle life data on other batteries

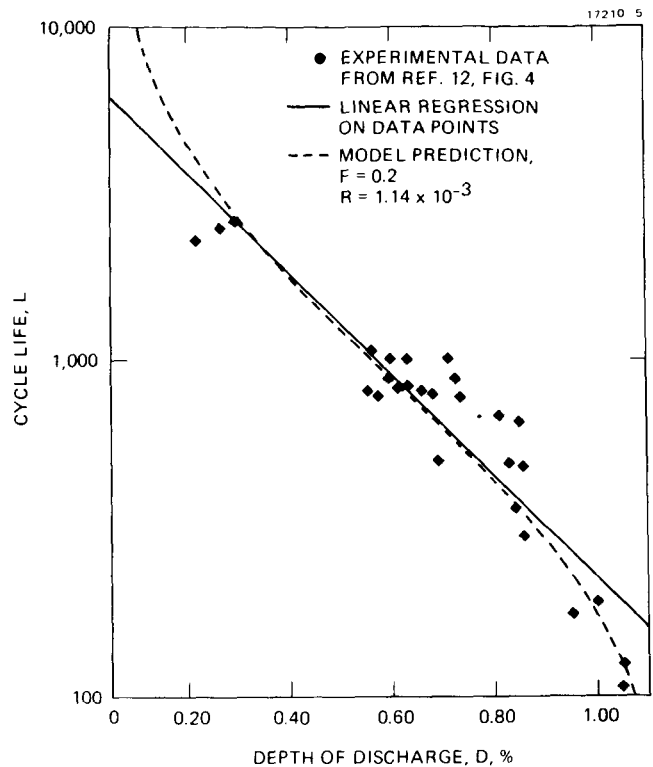


Fig. 5 Cycle life versus DOD of Li/MoS₂ cells.

such as nickel-zinc and lead-acid because we were not convinced that they fail gradually. Most reported values of α for those batteries¹ fall outside the range predicted by equation (4). They might represent catastrophic failure of the batteries.

The proposed model is based on the assumption that cell capacity is reduced at a constant rate per cycle. Unfortunately, existing data on cell capacity as a function of cycle life for Ni/Cd and Li/MoS₂ cells are unsuitable for testing that assumption. Though data are available on capacity as a function of cycle number for Ni/H₂ cells,^{13,14} their capacity was not measured in the same regime as that of cycling. The cycling regime of that test was a 45-min low earth orbit (LEO), whereas capacity was measured using the charge and discharge rates of a 90-min LEO regime. The resulting capacity data did not show a constant rate of capacity reduction. Some cells showed a roughly linear decrease¹³ and others showed a clearly nonlinear decrease.¹⁴ In another experiment, conducted by HRL, a sintered nickel electrode was cycled at 100% depth of discharge in a flooded 26% KOH electrolyte. The change in its capacity was roughly linear with the number of cycles, as shown in Fig. 6, supporting the assumption of the proposed model.

Equation (4) implies that the dependence of cycle life on DOD is not affected

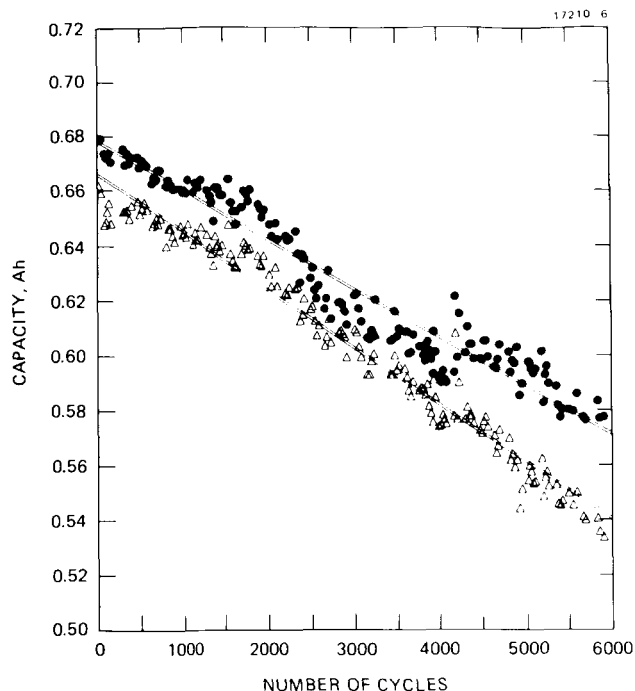


Fig. 6 Nickel electrode capacity versus number of cycles at 100% DOD in flooded cell with 26% KOH electrolyte for duplicate cells.

by cell design or the cell's intrinsic cycle life, and that, therefore, the relationship between cycle life and DOD is rigidly fixed. Improved cell design and intrinsic cycle life are related only to the value of R . For example, as shown in Fig. 7, variations in intrinsic cycle life for different types of cells result in vertical displacements of curves plotting cycle life as a function of DOD, without changing the curves' slopes or shapes. The figure also suggests that a meaningful accelerated cycle life test using a higher value of DOD than that of an actual mission can be carried out at considerable savings in time and cost.

The relative positions of the curves in Fig. 7 clearly show the cells' relative cycle life merits. Improved Ni/Cd cells using zirconia separators (curve C) have much longer cycle lives than do the cells containing nylon separators (curve B), now in use. A recent study¹⁴ showed that the cycle life of a Ni/H₂ cell with an improved electrolyte (26% KOH) is several times longer than that of a similar cell containing the current standard electrolyte of 31% KOH. A predicted minimum cycle life of the cell with the improved electrolyte is shown by curve D, whereas a predicted cycle life for a current standard Ni/H₂ cell should be close to curve C.

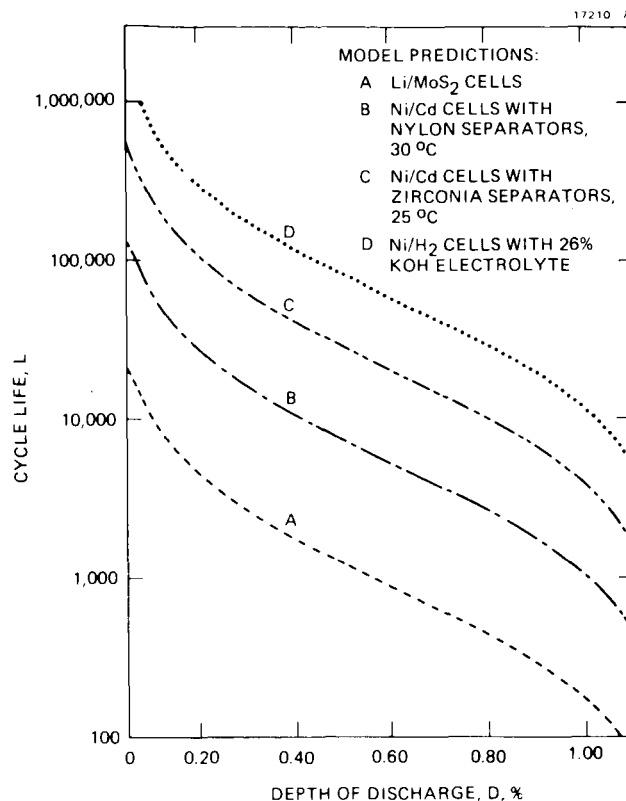


Fig. 7 Cycle life versus DOD for various cell types.

The mechanisms that cause a gradual loss of capacity are not yet well understood. However, it is clear that even the most advanced cells suffer from subtle morphological changes and chemical degradation over time. As those processes are identified, real improvements in electrochemical devices should follow. Modeling of cycle life as a function of depth of discharge, based on the results of accelerated testing, will be a valuable tool for prompt evaluation of those improvements.

VII. Conclusions

The proposed model appears to be more useful than those presented earlier,¹⁻⁴ though it too has flaws. The results discussed here support the following conclusions:

- When a cell fails because of a gradual loss of capacity (wearout), the relationship between cycle life and depth of discharge is rigidly fixed. Thus, meaningful accelerated cycle life testing can be performed at considerable savings in time and cost.

- Though the slope of a typical cycle-life-versus-DOD plot suggests that cycle life should roughly double with each 20% reduction in the DOD of cycling, cycle life can also be improved without reducing DOD by the use of advanced components and design. This paper includes the results of tests on experimental cells incorporating improved (chemically resistant) separator materials, rather than the nylon separators now standard in aerospace Ni/Cd cells. The improved separators do not affect cycle life in a way that changes the slope of the plot, but do cause a vertical displacement of the curve (as shown in Fig. 7) by an amount proportional to the improvement in the rate of capacity loss.

Some of the Ni/H₂ cell cycling test results suggest that a better (lower) value of R may derive from the use of alternative electrolyte compositions to achieve more favorable energy densities and cycle lives for future Ni/H₂ cells.

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